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Predicting Carbonate Species Ionic Conductivity in Alkaline Anion Exchange Membranes

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Abstract: Advances in membrane synthesis techniques have produced polymer electrolyte membranes that are capable of transporting anions in alkaline membrane fuel cells (AMFCs). These anion exchange membranes (AEMs) are being considered for use in portable power applications. One of the challenges with AEMs is the presence of carbonate and bicarbonate, which can replace hydroxide ions in the membrane, reducing the ionic conductivity. An experimental water permeation technique that has been developed by our lab is used to predict hydroxide ionic conductivity in AEMs [1,2]. Using this method, the ionic conductivity of the membrane can be predicted for AEMs with carbonate and bicarbonate species present. Predicted results are validated using values for AEM ionic conductivity previously reported in the literature.

Keywords: Alkaline anion exchange membrane; ionic conductivity; carbonate; bicarbonate; fuel cell.

Introduction

The AMFC uses an alkaline polymer membrane electrolyte. Because of the alkaline conditions, the AMFC is capable of operating on hydrogen or alcohol fuels and can use non-platinum catalyst alternatives including metals such as silver or nickel, among others [3-5]. AMFCs transport hydroxide ions from the cathode to the anode, which should reduce fuel crossover. Materials and synthesis procedures have improved; however, substantial challenges regarding the thermal, chemical and mechanical stability, as well as the ionic conductivity, of these AEM materials still need to be addressed [5-8].

Water is an electrochemical reaction product in AMFCs, and its presence is important to the performance of the cell. The ions transport through a hydrated membrane through several mechanisms including site hopping between the functional groups as well as bulk (en masse or vehicular) diffusion and the Grotthuss mechanism in the bulk pore. The ionic conductivity in the membrane has been shown to be proportional to the membrane hydration. If the water content is too low, ions cannot be effectively transported

through the membrane and the membrane conductivity approaches zero. This is often termed a percolation limit. For these reasons, water and its transport in the membrane have been extensively studied [9-13].

Water transport in proton exchange membranes (PEMs) has been extensively studied. Water diffusion in the membrane can be measured using various methods such as but not limited to absorption techniques [14-16], nuclear magnetic resonance [11,12], and permeation techniques [17,18]. Unfortunately, the range of values for the diffusion coefficients determined with these unique studies can span an order of magnitude between methods [19]. Each technique has its own advantages and deficiencies. The effort reported in this study used a permeation based method to calculate the diffusion coefficient of water in the membrane. This approach was selected because it is intuitive to understand and it most closely simulated the environment which would be seen during fuel cell operation.

The diffusion coefficient and conductivity of the membrane are highly dependent on local hydration, λ , in the membrane. The hydration of the membrane can be defined as the ratio of water molecules to the fixed charge carriers in the membrane (i.e., mol H₂O / mol equiv). As the membrane hydration increases the pores tend to open as the membrane swells, thereby allowing for a bulk diffusion region and greater dissociation of ions [10]. The diffusion coefficient tends to increase with hydration however there is a local maximum at lower hydrations. This non-linear behavior is due to a correction in activity coefficients due to non-ideal mixtures in the membrane, referred to as the Darken factor [20].

Typically, the membranes' ionic conductivity is also proportional to the hydration [11]. More recent AEMs developed have reported conductivity measurements that are roughly an order of magnitude less than that of PEMs [6,7,21]. The reasons for the decrease in conductivity are attributed to increased activation energies, decreased dissociation of the charge carriers, and decreased mobility

of the counter-ions [7,22]. To better understand the conductivity in the membrane, groups have used the dusty fluid model (DFM) to model ion transport [2,9,23,24]. This method has been used previously with both PEM and AEM fuel cells and demonstrated its ability to accurately predict ionic conductivity [2,9,24].

A challenge in AEM derived fuel cells is the presence of carbon dioxide (CO_2) which can lead to carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) formation. Small concentrations of carbon dioxide have been reported to significantly decrease the performance of AEM fuel cells [25]. The conversion from a hydroxide membrane to a carbonate/bicarbonate based membrane is rapid and there is a complete removal of hydroxide species within 30 minutes [26]. This is from the production of carbonate/bicarbonate species which have a lower diffusion coefficient in the membrane than the more mobile hydroxide ions.

Experiment

An Excellion I-200 (SnowPure, San Clemente, CA) AEM has been studied for this work. This membrane has a polypropylene based backbone with benzyl-trimethylammonium fixed charge carriers. Because of chemical stability concerns, the membrane was delivered in the chloride form. To exchange the membrane to a hydroxide form, the membrane was soaked in 10^{-4} M potassium hydroxide solution for 24 hours. This duration was selected because soaking the membrane for longer periods of time have shown the conductivity stabilizes after this period. Higher concentrations of potassium hydroxide can be used for the ion exchange process; however the membrane was shown unstable in 1 M potassium hydroxide solutions [27]. After conversion, the membrane was rinsed and soaked in deionized water to remove any excess potassium hydroxide. The membrane was then soaked in the deionized water for 48 hours with a water change after 24 hours. While being soaked, the solution was covered to prevent debris from falling in and was exposed to carbon dioxide in the air. To validate the experimental facility and practices, tests were initially run with a Nafion 117 PEM. Nafion 117 was supplied by Ion Power (New Castle, DE) and received in the proton form. The membrane was soaked in deionized water to hydrate the membrane. Installing the fully hydrated membrane does not affect the results because the experiment was allowed to reach steady state before data was collected. To isolate diffusion of water in the membrane, no gas diffusion or catalyst layers were used.

The diffusion coefficient of water through the membrane was found using a previously described water permeation method [1,24,28]. A concentration gradient of water vapor was created across the membrane and the water flux was measured using desiccants. This provided an experimentally simple and effective way of measuring the water diffusion coefficient. The water flux was measured

in order to find water diffusion coefficients in the membrane. This is important so that the water content in the membrane can be modeled as well as relating the diffusion coefficient of hydroxide ions in the membrane. The diffusion coefficient is dependent on the local water content in the membrane.

With the flux measurements, the data was processed using a water flux model to model the experimental conditions. A minimization algorithm was utilized to find a diffusion coefficient that reduced the error between the experimental results and the water flux model. The experiment was validated with a well-studied membrane, DuPont Nafion 117 PEM and had reasonable agreement. The membrane of interest for this study was SnowPure Excellion I-200 AEM.

Numerical Modeling

With an understanding of the water diffusion coefficient and local water content in the membrane, ionic transport can be examined. The size of the mobile species is similar to that of water. In an AMFC, the mobile species is a hydroxide ion (OH^-) and in a PEM fuel cell, the proton is solvated with a water molecule forming hydronium (H_3O^+) [2,9]. It is more difficult to measure the transport of these ions in the membrane so it can be assumed that the hydroxide ions have the same diffusion coefficient as water in the membrane.

To calculate the ionic conductivity, a relationship using the DFM and Ohm's law can be used. Based on a Stefan-Maxwell diffusion model, the DFM assumes that there are large "dust" particles with zero velocity. The membrane can be assumed to be these large particles which are uniformly distributed in space. This means that the fixed charge carriers are also uniformly distributed. To maintain electroneutrality, it is assumed that there is no chemical potential gradient of ions in the system. Given that the only two mobile species are water and hydroxide, an equation for conductivity can be derived if equimolar counter diffusion is assumed between the two species. This equimolar counter diffusion assumption is not necessarily valid given an operating fuel cell which would need to include electro-osmotic drag and water production and consumption. However, assuming that local pseudo equilibrium exists, equimolar counter diffusion can be used as an approximation to arrive at Eq. 1.

$$\sigma = \frac{z_i^2 F^2}{RT} \left[\frac{D_{i,H_2O}^e}{1 + \delta_i} \right] C_i \quad [1]$$

The conductivity is found using several constants including the ion valence, z_i , Faraday's constant, F , the universal gas constant, R , and temperature, T . The effective diffusion coefficient between species i and water, D_{i,H_2O}^e , is taken as the diffusion coefficient of the two species in infinite

dilution, D_{i,H_2O}^0 , and then multiplied by a correction factor such that $D_{i,H_2O}^e = (\varepsilon - \varepsilon_0)^q D_{i,H_2O}^0$ [13,29]. The correction factor takes into account the pore volume fraction of water in the membrane, ε , and a percolation limit, ε_0 , which is a minimum hydration necessary to support transport of ions. The Bruggemann exponent, q , is a fitted parameter used to fit to experimental data where a value of $q = 1.5$ is typically used. The membrane diffusion coefficient for the mobile ion is contained in the δ term. This term is defined as a ratio of the effective diffusion coefficient between water and hydroxide and the membrane and hydroxide as seen in Eq. 2.

$$\delta_{OH} = \frac{D_{OH,H_2O}^e}{D_{OH,M}^e} \approx \frac{1}{\lambda} \frac{D_{OH,H_2O}^0}{D_{OH,M}^0} \quad [2]$$

When the mobile species is water, the proper values can be substituted into Eq. 2 and δ is calculated. If the mobile species is another ion, i , then some manipulation needs to be performed in order to find δ . In order to get the proper ratio of ion-water to ion-membrane diffusion coefficients, Eq. 2 is multiplied by two terms, as seen in Eq. 3. The first term is a ratio of diffusion coefficients in infinite dilution. This eliminates the hydroxide-water diffusion coefficient leaving only the diffusion coefficient of the ion of interest, i , and water. The final term is a ratio of ion-membrane diffusion coefficients. This term is found using kinetic gas theory and is predicted with reduced mass, collision cross sectional area and number density. With the addition of these two terms to Eq. 2, δ values for different ions can be calculated.

$$\delta_i = \frac{1}{\lambda} \frac{D_{OH,H_2O}^0}{D_{OH,M}^0} \frac{D_{i,H_2O}^0}{D_{OH,H_2O}^0} \frac{D_{OH,M}}{D_{i,M}} \quad [3]$$

The concentration of mobile ions in the membrane is also required for calculating the conductivity. The concentration of ions is dependent on the hydration of the membrane which will define how much volume the ions can be dissolved into. The concentration of ions can be defined by C_i and is dependent on hydration and the molar volume of the membrane, $\bar{V}_M = EW/\rho$ where EW is the equivalent weight and ρ is the density of the membrane. At low hydrations, the concentration of ions is high; however, dissociation of hydroxides from the fixed charge carriers may suffer at low hydration [22]. For the carbonate cases, the dissociation is not known for these membranes. Therefore, the complete dissociation is assumed even though this will predict values that are greater than the true values.

When multiple ionic species are present in the membrane, the ions will interact. However, these diffusion effects can be assumed negligible given that the membrane or “dust” particles are much larger than that of the other mobile

species. With these conditions, the diffusion coefficients of the mobile species to the membrane would be much more significant and would have the largest effect on the ionic conductivity. In addition to this, it is assumed that the ionic conductivities of each species can be combined to find a total ionic conductivity of the membrane given the concentrations of each species.

Results and Discussion

Modeling the ionic conductivity of hydroxide ions in SnowPure Excellion I-200 has been demonstrated [24]. Changing the mobile ion to carbonate and bicarbonate was shown experimentally to decrease the ionic conductivity of the membrane. With only hydroxide ions present, the ionic conductivity was reported to be 3.5 mS/cm. The ionic conductivity decreased to 2.25 mS/cm when an ion exchange was performed with carbonate and bicarbonate ions.

Numerical predictions were obtained over a range of hydration values to find ionic conductivities with equal concentrations of carbonate and bicarbonate ions. This was performed to match experimental results from Vega et al [27]. In their experiment, a solution of 0.5 M Na_2CO_3 and 0.5 M NaHCO_3 was used in the ion exchange of the membrane. This produces equal concentrations of carbonate and bicarbonate in solution. Since the membrane is soaked in this solution, it is assumed that the equal concentrations of each are present in the membrane. There are also hydroxide ions present in the membrane however the concentration of hydroxide ions should be negligible; they have been exchanged by the less mobile carbonate/bicarbonate ions.

The ionic conductivity results from Eq. 1 can be seen in Table 1. It can be seen that the carbonate ion contributes to most of the ionic conductivity in the membrane. This can be partially attributed to a smaller diffusion coefficient of carbonate than bicarbonate in the membrane. This may be explained by using approximations from kinetic gas theory. Kinetic theory tells us that a (lighter) smaller radius particle is able to diffuse more easily through a second species or medium. In this case, it diffuses more easily through the membrane, thus increasing its ionic conductivity. Also, the carbonate ion carries a charge of $z = -2$ while the bicarbonate only carries a charge of $z = -1$. This allows for more charge to be transported across the membrane for the same number of carbonate ions than bicarbonate ions.

Table 1. Comparing the individual contributions for each ion to the experimental result at fully hydrated conditions.

	CO_3^{2-}	HCO_3^-	Total	Vega et al. [27]
Conductivity (mS/cm)	3.0	0.5	3.5	2.3

Because of its negligible concentration, the contribution from the hydroxide ion is negligible for these conditions.

Conclusions

The presence of carbonates in AEMs has been studied showing the relationship of how the ionic conductivity will decrease with an increasing concentration. The individual contributions from each ion have been calculated and agree with the expected results for the total membrane ionic conductivity. This model does not consider changes in the composition of the membrane which has been shown to happen as the operating conditions change for the fuel cell.

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